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Bipolar resistive switching properties of microcrystalline TiO_2 thin films deposited by pulsed laser deposition

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ABSTRACT

TiO_2 thin films were deposited on ITO (indium–tin-oxide)-buffered glass by pulsed laser deposition. Bipolar resistive switching behaviors of Ag/microcrystalline TiO_2/ITO stacked structures were systematically investigated. Dependence of switching voltage and band gap energy on deposition temperature were also analyzed. Results indicate that the reset voltages and band gap energy (E_g) vary from −0.9 V to −6.8 V and 3.26 eV to 3.18 eV respectively, while the TiO_2 films were formed from 300 °C to 600 °C. These bipolar switching phenomena have been also discussed based on the Schottky barrier at the Ag/TiO_2 interface structure.

1. Introduction

Resistive switching and voltage controlled negative differential resistance phenomena have been observed since the 1960s [1]. In recent years, resistive switching in simple binary transition metal oxide (TMO) thin films, such as NiO and TiO_2, attracts great interests for possible applications in nonvolatile memory devices [2–14]. Compared to more complex materials such as $Pr_{1-x}Ca_xMnO_3$ [15,16], $La_{1-x}Ca_xMnO_3$ [17] or Cr-doped $SrZrO_3$ [18], these simple binary oxide TMO materials exhibit advantages not only in their relative simple fabrication process, but also in their compatibility with CMOS processes. As for switching mechanism, many studies attributed it to filament conduction theory which is closely related to the formation and rupture of conducting filaments [6,9]. It is assumed that the filaments are formed by percolation of some kind of defects. In TiO_2, the most probable defects are titanium interstitials or oxygen vacancies. However, the exact nature of the filaments and the actual mechanism of resistive switching in TiO_2 films have not been clearly understood yet.

Although the nature of the resistance change produced by applying a unipolar or bipolar voltage has not yet been characterized in detail, many studies have been done to explain the bipolar resistance switching behaviors. Fujimoto et al. [14] reported that the Mott transition in the nanoactive TiO_2 layer adjacent to the top Pt electrode properly explained the switching polarity of the memory cell. However, Tsunoda et al. [19] suggested that the bipolar switching phenomena could be ascribed to the formation and rupture of a filamentary conductive path which consists of a chain of Ag atoms. Whereas in complex materials such as $Pr_{1-x}Ca_xMnO_3$, the resistance change produced by applying a bipolar voltage pulse to $Pr_{1-x}Ca_xMnO_3$ is ascribed to a Schottky barrier formed at the metal–insulator interface by carrier trapping levels [20,21].

In this work, we investigated the influence of the temperature on the resistive switching properties and the optical properties of the TiO_2 thin films, and found that the TiO_2 thin films with Ag electrodes exhibited a bipolar characteristic. In addition, an increase of the deposition temperatures between 300 °C and 600 °C led to a decrease of the band gap energy (E_g). The band gap evolution of the TiO_2 thin films might be attributed to the electronic disorder due to oxygen deficiency at a higher oxidation temperature [22].

2. Experimental details

The TiO_2 films employing a stoichiometric ceramic TiO_2 target were grown on commercial conducting ITO (indium–tin-oxide)-buffered glass substrates by a pulsed laser deposition technique. The substrate temperatures were varied from 300 °C to 600 °C under 20 Pa oxygen pressures during ablation. After deposition, the film was cooled to the ambient temperature in one atmosphere of oxygen. Ag top electrode with diameter of 1.0 mm was formed by

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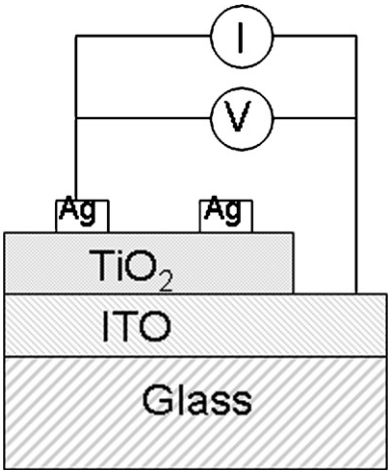

Fig. 1. Schematic view of the sample and the overall circuit arrangement used in the measurement of the electrical characteristics.

mask printing and curing (200 °C for 20 min) of Ag-loaded epoxy paste to acquire a high electrical conductivity.

A schematic diagram of the device structure and the measurement circuit is shown in Fig. 1. Current–voltage (I–V) characteristics were examined by Kerthley 2410c source meter unit. Current flows from Ag to ITO electrode in positive bias and vice versa in negative bias. Scanning electron microscopy (SEM) was employed to characterize the morphology of as-grown films. An UV–visible transmittance spectra was used to characterize the optical properties of the resulting TiO_2 films.

3. Results and discussion

Fig. 2 displays the cross-section and top view SEM images of the TiO_2 films deposited at 400 °C under 20 Pa oxygen ambient pressures. The microstructure of TiO_2 layer is probably like microcrystalline consisting of columnar grains (see Fig. 2a for a 100 nm thick film) with in-plane grain diameters from 20 nm to 50 nm (see Fig. 2b).

Fig. 3 represents the typical I–V characteristics of Ag/TiO_2/ITO structures during a linear voltage sweep. The voltage is applied to the Ag electrode while the ITO electrode is grounded. As the applied voltage increases from zero to positive, a sudden decrease in resistance from a high-resistance state (HRS) to a low-resistance state (LRS), the so-called set process, occurs at 2.5 V without forming (the arrow denoted "2" in Fig. 3). The current compliance in the set process is limited to 10 mA. The LRS is stable even after removal of the applied voltage. As the applied voltage increases from zero to positive again, there is no sudden change in resistance. But if the applied voltage is swept from zero to negative bias after the set, the resistance increases abruptly from the LRS to the HRS at −1.8 V (the arrow denoted "5" in Fig. 3), the so-called reset process. This cycle exhibits a so-called bipolar behavior which is different from a unipolar behavior that reported by other authors [9,10]. Both the bipolar and unipolar switching are mostly thought to be attributed to filament conduction theory which is closely related to formation and rupture of conducting filaments [9,11–14,19].

So far, it was suggested that bipolar switching could be due to an explicit asymmetry such as a poling (training) of the oxide produced by large electric pulses [23]. Hosoi et al. has demonstrated that the bipolar switching seen in an apparently symmetric sandwich can be turned into a unipolar one by introducing the external asymmetry [24]. The bipolar behavior in Ag/TiO_2/ITO stacked structures also could be ascribed to the external asymmetry. As a bipolar behavior is also found in Ag/TiO_2/Pt structures in our experiment,

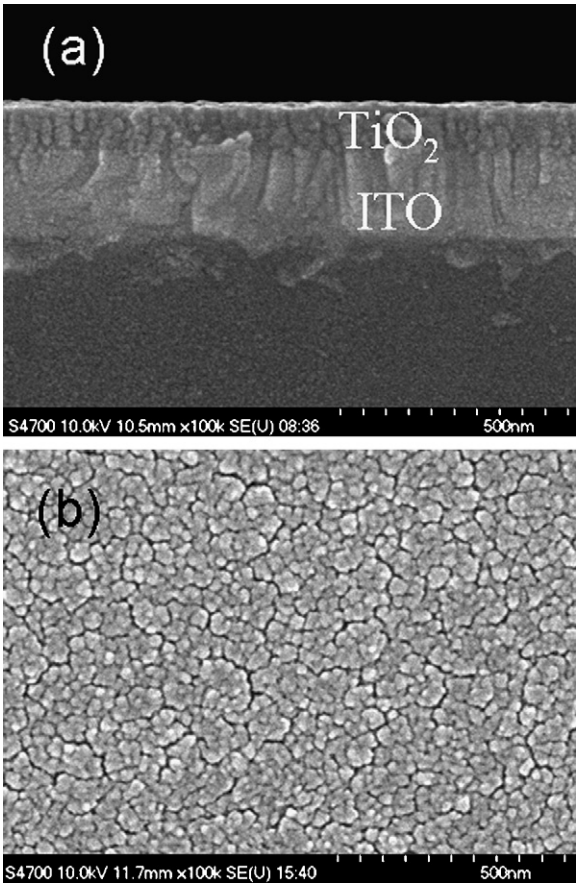

Fig. 2. SEM images of TiO_2 films deposited at 400 °C under 20 Pa oxygen ambient pressures. (a) Cross-section and (b) top view.

we can assume that this bipolar behavior in Ag/TiO_2/ITO stacked structures is mainly attributed to the Ag/TiO_2 interface. According to the Schottky contact model, when a metal-oxide contact is formed, the characteristics of contact can be simply determined by the difference between the metal work function and the Fermi level of a semiconductor. As the work function of TiO_2 is less than that of the Ag, a Schottky barrier can be formed at the Ag/TiO_2 interface, after "set" process during a positive linear voltage sweep, a same bias voltage cannot make it achieve the "reset" process due to the Schottky barrier. On the other hand, application of negative bias voltage could make the current to reach the "reset" value without the Schottky barrier. This resistance switching behavior

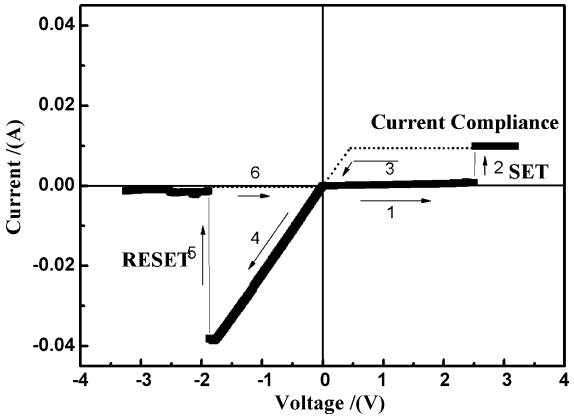

Fig. 3. Typical I–V curves of Ag/TiO_2/ITO structure obtained during successive resistance switching measurements with a current compliance of 10 mA.

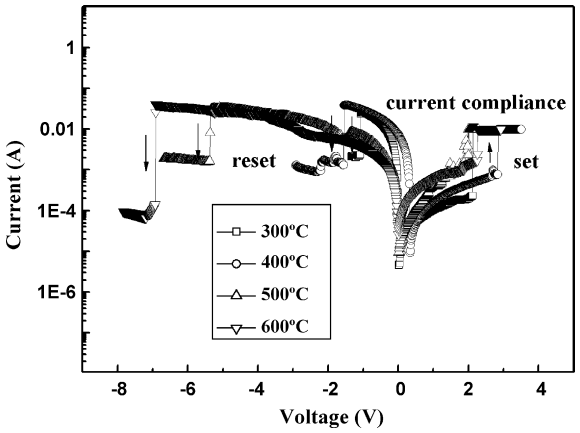

Fig. 4. Bipolar resistive switching characteristics of the TiO_2 films deposited at different temperatures from 300 °C to 600 °C under 20 Pa oxygen ambient pressures measured at room temperature.

exhibits polarity characteristics. The Schottky barrier at the Ag/TiO_2 interface explains the switching polarity of the memory cell.

Fig. 4 shows the typical *I–V* characteristics of TiO_2 films deposited at different temperatures from 300 °C to 600 °C during a linear voltage sweep. They are shown in both cases for logarithmic scale. It is found that the reset voltages vary from −0.9 V to −6.8 V with the deposition temperature increasing from 300 °C to 600 °C, whereas the set voltages do not exhibit obvious dependence on the deposition temperature, as shown in Fig. 5. The value of R_H/R_L is defined as resistance change ratio, which is obviously influenced by the deposition temperature. For the sample prepared substrate temperature of 400 °C, the resistance change ratio can reach about 500, as shown in Fig. 6, which is attributed to varies of both R_H and R_L. It is assumed that a proper concentration of defects in TiO_2 film such as oxygen vacancies (V_O^{2+}) and Ti interstitials (Ti_i^{4+}) is needed to obtain a large resistance change ratio.

In order to investigate the change of the concentration of defects in TiO_2 films, we characterized the optical properties of the resulting TiO_2 films deposited at different temperatures. When the temperature is increased from 300 °C to 600 °C, the value of E_g decreased from 3.26 eV to 3.18 eV, as shown in Fig. 7. This is consistent with the change of initial resistance (measured at 0.1 V) of TiO_2 films. An increase in the deposition temperatures between 300 °C and 600 °C led to a decrease in the initial resistances. It is reasonable to assume that the oxygen deficient TiO_2 film is much more conducting than the stoichiometric one irrespective of whether the

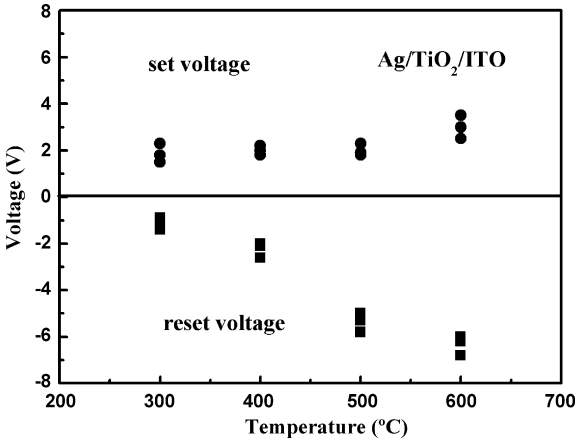

Fig. 5. 'Set' and 'reset' voltages for *V*-sweep measurements of Ag/TiO_2/ITO samples, plotted against the deposition temperature.

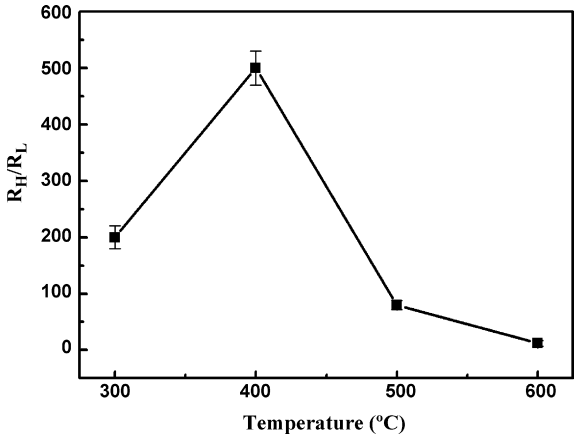

Fig. 6. Resistance change ratios (R_H/R_L) of the TiO_2 films deposited at different temperatures from 300 °C to 600 °C under 20 Pa oxygen ambient pressures.

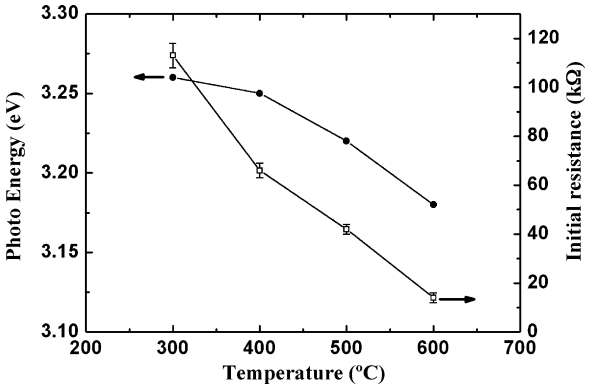

Fig. 7. Band gap energy (E_g) and initial resistances for the TiO_2 films deposited at different temperatures.

major defect type is oxygen vacancies (V_O^{2+}) or Ti interstitials (Ti_i^{4+}) [25]. It is considered that oxide films fabricated at high temperature contains fewer deficiencies attributing to the improvement of crystallinity. However, on the other hand, because of the low vacuum, high temperature can result in the decomposition of formed TiO_2 films or the breaking away of oxygen atoms in TiO_2 films. Thus, the band gap evolution of the films is probably attributed to the electronic disorder due to oxygen deficiency at higher deposition temperature.

4. Conclusions

In summary, bipolar resistive switching behaviors have been found and evaluated in Ag/TiO_2/ITO structures in which microcrystalline TiO_2 film was formed by the pulsed laser deposition at different growth temperature from 300 °C to 600 °C. The resistance ratio can reach about 500 at the deposition temperature of 400 °C due to a proper concentration of defects in TiO_2 film. The bipolar resistive switching phenomenon could be ascribed to the Schottky barrier at the Ag/TiO_2 interface. A same bias voltage cannot make it achieve the "reset" process due to the Schottky barrier.

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References

[1] S.R. Ovshinsky, Phys. Rev. Lett. 21 (1968) 1450.
[2] S. Seo, M.J. Lee, D.H. Seo, E.J. Jeoung, D.-S. Suh, Y.S. Joung, I.K. Yoo, I.R. Hwang, S.H. Kim, I.S. Byun, J.-S. Kim, J.S. Choi, B.H. Park, Appl. Phys. Lett. 85 (2004) 5655.
[3] S. Seo, M.J. Lee, D.H. Seo, S.K. Choi, D.-S. Suh, Y.S. Joung, I.K. Yoo, I.S. Byun, I.R. Hwang, S.H. Kim, B.H. Park, Appl. Phys. Lett. 86 (2005) 093509.
[4] S. Seo, M.J. Lee, D.C. Kim, S.E. Ahn, B.-H. Park, Y.S. Kim, I.K. Yoo, I.S. Byun, I.R. Hwang, S.H. Kim, J.-S. Kim, J.S. Choi, J.H. Lee, S.H. Jeon, S.H. Hong, B.H. Park, Appl. Phys. Lett. 87 (2005) 263507.
[5] D.C. Kim, S. Seo, S.E. Ahn, D.-S. Suh, M.J. Lee, B.-H. Park, I.K. Yoo, I.G. Baek, H.-J. Kim, E.K. Yim, J.E. Lee, S.O. Park, H.S. Kim, U-In. Chung, J.T. Moon, B.I. Ryu, Appl. Phys. Lett. 88 (2006) 202102.
[6] D.C. Kim, M.J. Lee, S.E. Ahn, S. Seo, J.C. Park, I.K. Yoo, I.G. Baek, H.J. Kim, E.K. Yim, J.E. Lee, S.O. Park, H.S. Kim, U-In. Chung, J.T. Moon, B.I. Ryu, Appl. Phys. Lett. 88 (2006) 232106.
[7] K. Kinoshita, T. Yamura, M. Aoki, Y. Sugiyama, H. Tanaka, Appl. Phys. Lett. 89 (2006) 103509.
[8] K. Jung, H. Seo, Y. Kim, H. Im, J.P. Hong, J.-W. Park, J.-K. Lee, Appl. Phys. Lett. 90 (2007) 052104.
[9] B.J. Choi, D.S. Jeong, S.K. Kim, C. Rohde, S. Choi, J.H. Oh, H.J. Kim, C.S. Hwang, K. Szot, R. Waser, B. Reichenberg, S. Tiedke, J. Appl. Phys. 98 (2005) 033715.
[10] C. Rohde, B.J. Choi, D.S. Jeong, S. Choi, J.S. Zhao, C.S. Hwang, Appl. Phys. Lett. 86 (2005) 262907.
[11] D.S. Jeong, H. Schroeder, R. Waser, Appl. Phys. Lett. 89 (2006) 082909.
[12] B.J. Choi, S. Choi, K.M. Kim, Y.C. Shin, C.S. Hwang, S.-Y. Hwang, S. Cho, S. Park, S.-K. Hong, Appl. Phys. Lett. 89 (2006) 012906.
[13] K.M. Kim, B.J. Choi, D.S. Jeong, C.S. Hwang, S. Han, Appl. Phys. Lett. 89 (2006) 162912.
[14] M. Fujimoto, H. Koyama, M. Konagai, Y. Hosoi, K. Ishihara, S. Ohnishi, N. Awaya, Appl. Phys. Lett. 89 (2006) 223509.
[15] A. Asamitsu, Y. Tomioka, H. Kuwahara, Y. Tokura, Nature (Lond.) 50 (1997) 388.
[16] S.Q. Liu, N.J. Wu, A. Ignatiev, Appl. Phys. Lett. 76 (2000) 2749.
[17] L. Huang, B.J. Qu, L.T. Liu, L.W. Zhang, Solid State Commun. 143 (2007) 382.
[18] Y. Watanabe, J.G. Bednorz, A. Bietsch, Ch. Gerber, D. Widmer, A. Beck, S.J. Wind, Appl. Phys. Lett. 78 (2001) 3738.
[19] K. Tsunoda, Y. Fukuzumi, J.R. Jameson, Z. Wang, P.B. Griffin, Y. Nishi, Appl. Phys. Lett. 90 (2007) 113501.
[20] A. Sawa, T. Fujii, M. Kawasaki, Y. Tokura, Appl. Phys. Lett. 85 (2004) 4073.
[21] T. Fujii, M. Kawasaki, A. Sawa, H. Akoh, Y. Kawazoe, Y. Tokura, Appl. Phys. Lett. 86 (2005) 012107.
[22] C.-C. Ting, S.-Y. Chen, D.-M. Liu, J. Appl. Phys. 88 (2000) 4628.
[23] A. Baikalov, Y.Q. Wang, B. Shen, B. Lorenz, S. Tsui, Y.Y. Sun, Y.Y. Xue, C.W. Chu, Appl. Phys. Lett. 83 (2003) 957.
[24] Y. Hosoi, et al., Technical Digest International Electronic Devices Meeting, IEEE, New York, 2006, p. 793.
[25] K.M. Kim, B.J. Choi, C.S. Hwang, Appl. Phys. Lett. 90 (2007) 242906.